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14. ABSTRACT

The focus of this research was on introducing advanced concepts from laser technology, controlled quantum dynamics and specialize software to address the problem of detecting chemical and biological agents. This research was initiated at the time when the confluence of these techniques and concepts was beginning to see success in various laboratories. The research performed during the MURI involved a number of interrelated activities concerning optical detection and mass spectrometry with shaped laser pulses acting as a special family of tailored “photonic reagents”. The research ranged from basic theoretical developments in the subject of controlling quantum phenomena out through enhancement of the associated

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Report Title

MURI: Optimal Quantum Dynamic Discrimination of Chemical and Biological Agents

Final Report

ABSTRACT

The focus of this research was on introducing advanced concepts from laser technology, controlled quantum dynamics and specialize software to address the problem of detecting chemical and biological agents. This research was initiated at the time when the confluence of these techniques and concepts was beginning to see success in various laboratories. The research performed during the MURI involved a number of interrelated activities concerning optical detection and mass spectrometry with shaped laser pulses acting as a special family of tailored "photonic reagents". The research ranged from basic theoretical developments in the subject of controlling quantum phenomena out through enhancement of the associated laser technology and a variety of key experiments demonstrating the concepts. The research in the MURI made significant advances in laying a rigorous foundation for the creation of a new class of non-linearly functioning detectors of chemical and biological agents. Future R&D in non-linear detection should be able to build on these foundations and take this subject to an advanced level for technology transfer. A summary of these advances under the MURI is given below.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Quantum Wavefunction Controllability, G. Turinici and H. Rabitz, Chem. Phys., 267, 1-9 (2001).

Theoretical Considerations for Laser Control of Quantum Systems, H. Rabitz, in Encyclopedia of Modern Optics, J.E. Midwinter, A. Miller, and L. Bayvel, eds., Academic Press, United Kingdom (2001).

Closing the Loop on Bond Selective Chemistry Using Tailored Strong Field Laser Pulses, R.J. Levis and H. Rabitz, J. Phys. Chem. A, 106, 6427-6444 (2002).

Some mathematical and algorithmic challenges in the control of quantum dynamics phenomena, E. Brown and H. Rabitz, J. Math. Chem., 31, 17-63 (2002).

Optimal Dynamical Discrimination of Similar Molecules Through Quantum Learning Control, B. Li, G. Turinici, V. Ramakrishna and H. Rabitz, J. Phys. Chem. B, 106, 8125-8131 (2002).

An Investigation of the effects of Experimental Parameters on the Closed-loop Control of Photoionization/Dissociation Processes in Acetophenone, P. Graham, G. Menkir, R. Levis, Spec. Acta Part B-Atomic Spectro.. 58, 1097 (2003).

Nonadiabatic Dynamics of Polyatomic Molecules and Ions in Strong Laser Fields, A. Markevitch, S. Smith, N. Moore, H. Schlegel, D. Romanov, M. Ivanov and R. Levis, Phys. Rev. A,. 68, (2003).

A Local-Time Algorithm for Achieving Quantum Control, F.L. Yip, D.A. Mazziotti and H. Rabitz, J. Phys. Chem. A, 107, 7264-7268 (2003).

Quantum Control via Adaptive Tracking, W. Zhu and H. Rabitz, J. Chem. Phys., 119, 3619-3625 (2003).

Closed-Loop Quantum Control Utilizing Time Domain Maps, J.S. Biteen, J.M. Geremia and H. Rabitz, Chem. Phys., 290, 35-45 (2003).

Molecular alignment by trains of short laser pulses, M. Leibscher, I. Sh. Averbukh and H. Rabitz, Phys. Rev. Lett., 90, 213001-4 (2003).

The Role of Theory in the Laboratory Control of Quantum Dynamics Phenomena, H. Rabitz, Theoret. Chem. Accts., 109, 64-70 (2003).

Shaped Laser Pulses as Reagents, H. Rabitz, Science, 299, 525-527 (2003).

Quantum Physics under Control, I. Walmsley and H. Rabitz, Physics Today, 56, 43-49 (2003).

Quantum Optimally Controlled Transition Landscapes, H. Rabitz, M. Hsieh and C. Rosenthal, Science, 303, 998 (2004).

Shaped Laser Pulses Acting as Photonic Reagents, H. Rabitz, in Ultrafast Molecular Events in Chemistry and Biology, M. M. Martin and J. T. Hynes, eds. (Elsevier), 2004.

Mechanistic Analysis of Optimal Dynamic Discrimination of Similar Quantum Systems, A. Mitra and H. Rabitz, J. Phys. Chem. A., 108, 4778 (2004).

Optimal Discrimination of Multiple Quantum Systems: Controllability Analysis, G. Turinici, V. Ramakrishna, B. Li and H. Rabitz, J. Phys. A, 37, 273-282 (2004).

Optimal Control of Quantum Non-Markovian Dissipation: Reduced Liouville-Space Theory, R. Xu, Y.J. Yan, Y. Ohtsuki, Y. Fujimura and H. Rabitz, J. Chem. Phys., 120, 6600 (2004).

Cooperating or Fighting with Noise in the Optimal Control of Quantum Dynamics, F. Shuang, M. Dykman and H. Rabitz, J Chem. Phys., 121, 9270-9278 (2004).

Optimal Quantum Control with Multi-Polarization Fields, R. Wu, I. Solá, and H. Rabitz, Chem. Phys. Let, 400, 469-475 (2004).

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Fragmentation pathways in a series of CH3COX molecules in the strong field regime, S. Anand, M. Zamari, G. Menkir, and R. Levis, J. Phys. Chem. A, 108, 3162 (2004).

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Static and Dynamic Polarizabilities of Conjugated Molecules and their Cations, S. M. Smith, A. Markevitch, D. Romanov, X. Li, R. Levis and H. B. Schlegel, J. Phys. Chem. 108, 11063 (2004).

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Connectivity analysis of quantum control, R. Wu, H. Rabitz, G. Turinici and I. Sola, Phys. Rev. A, 70, 052507 (2004).

Femtosecond laser pulses distinguish bacteria from background urban aerosols, F. Courvoiser, V. Boutou, V. Wood, J.-P. Wolf, A. Bartelt, M. Roth, H. Rabitz, Appl. Phys. Lett, 87, 063901 (2005).

Time-Dependent Hartree-Fock Approach for Studying the Electronic Optical Response of Molecules in Intense Fields, X. Li, S.M. Smith, A. Markevitch, D. Romanov, R. Levis and H. B. Schlegel, Chem. Chem. Phys., 7, 233 (2005).

Cooperating or Fighting with Decoherence in the Optimal Control of Quantum Dynamics, F. Shuang and H. Rabitz, J. Chem. Phys., 124, 154105 (2006).

Quantum Optimal Control: Hessian analysis of the control landscape, Z. Shen, M. Hsieh and H. Rabitz, J. Chem. Phys., 124, 204106 (2006).

Exploring the level sets of quantum control landscapes, A. Rothman, T.-S. Ho and H. Rabitz, Phys. Rev. A, 73, 053401 (2006).

Quantum optimal control of molecular isomerization in the presence of competing dissociation channel, M. Artamonov, T.-S. Ho., H. Rabitz, J. Chem. Phys., 124, 064306, (2006).

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Teaching the environment to control quantum systems, A. Pechen, H. Rabitz, Phys. Rev. A, 73, 062102 (2006).

Observation-Assisted optimal control of quantum dynamics, F. Shuang, A. Pechen, T.-S. Ho, H. Rabitz, J. Chem. Phys., 126, 134303 (2007).

Adaptive control of the spatial position of white light filaments in an aqueous solution, G. Heck, J. Sloss, R. Levis, Opt. Com., 259, 216 (2006).

Rapid Proton Transfer Mediated by a Strong Laser Field, A. Markevitch, D. Romanov, S. Smith, and R. Levis, Phys. Rev. Lett., 96, 163002 (2006).

Assessing and managing laser system stability for quantum control experiments, M. Roth, J. Roslund, H. Rabitz, Rev. Sci. Inst. , 77, 083107 (2006).

Control Goal Selection through Anti-Correlation Analysis in the Detection Space. Huyen T. Tran, Dmitri A. Romanov, Robert J. Levis, J. Phys. Chem. A, 110, 10558 (2006).

Laboratory observation of quantum control level sets, J. Roslund, M. Roth, H. Rabitz, Phys. Rev. A, 74, 043414 (2006).

Probing strong-field electron-nuclear dynamics of polyatomic molecules using proton motion, A. Markevitch, D. Romanov, S. Smith, R. Levis, Phys. Rev. A. 75, 053402 (2007).

A numerical simulation of non-adiabatic electron excitation in the strong-field regime: 3. Polyacene Neutrals and Cations, S. Smith, X. Li,

A. Markevitch, D. Romanov, R. Levis, H. Schlegel, J. Phys. Chem. A. 111, 6920 (2007).

Adaptive femtosecond pulse shaping to control supercontinuum generation in a microstructure fiber, D. Lorenc, D. Velic, A. Markevitch, R. Levis, R. J., Opt. Comm., 276, 288 (2007).

Quantum control mechanism analysis through field based Hamiltonian encoding: A laboratory implementable algorithm, A. Mitra and H. Rabitz, J. Chem. Phys., 120, 044112 (2008).

Multicomponent Control via Shaped, Strong Laser Fields Mass Spectroscopy, L. Palliyaguru, J. Sloss, H. Rabitz, R Levis, J.Mod. Optics, 55, 177 (2008).

Adaptive reshaping of objects in (multiparameter) Hilbert space for enhanced detection and classification: an application of receiver operating curve statistics to laser-based mass spectroscopy, D. Romanov, D. Healy, J. Brady, R. Levis, J. Opt. Soc. Am. A., 25, (2008).

Measuring the spatiotemporal electric field of ultrashort pulses with high spatial and spectral resolution, P. Bowlan, P. Gabolde, M. Coughlan, R. Trebino, and R. Levis, J. Opt. Soc. Am. B, 25, (2008).

Identification of biological microparticles using ultrafast depletion spectroscopy, F. Courvoisier, L. Bonacinia, V. Boutou, B. Thuillier, J. Extermann, M. Roth, H. Rabitz and HP Wolf, Faraday Discuss., 137, 37, (2008).

Understanding the role of representation in controlled quantum-dynamical mechanism analysis, A. Mitra, I. Sola and H. Rabitz, Phys. Rev. A, 77, 043415 (2008).

Number of Papers published in peer-reviewed journals: 50.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

Number of Presentations:

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

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Number of Manuscripts: 0.00

Number of Inventions:

Graduate Students

NAME	PERCENT SUPPORTED
Baiqing Li	
Abhra Mitra	
Matthias Roth	
Richard Sharp	
Madhavan Narayanan	
Alexei Markevitch	
Muhannad Zamari	
Getahun Menkir	
Lalinda Palliyaguru	
Ryan Compton	
Matt Coughlan	
FTE Equivalent:	
Total Number:	**11**

Names of Post Doctorates

NAME	PERCENT SUPPORTED
Andreas Bartelt	
David Mazziotti	
Ignacio Solá	
Stanley Smith	
FTE Equivalent:	
Total Number:	**4**

Names of Faculty Supported

NAME	PERCENT SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

NAME	PERCENT SUPPORTED
Frank Yip	
Kate Moore	
Adam Rothman	
Benjamin Bui	
Ruth Elliott	
Josh Meyer	
Joseph Sloss	
Huyen Tran	
FTE Equivalent:	
Total Number:	**8**

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	8.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	8.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	8.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Baiqing Li
Abhra Mitra
Matthias Roth
Richard Sharp
Getahun Menkir
Muhannad Zamari
Total Number: 6

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

MURI: Optimal Quantum Dynamic Discrimination of Chemical and Biological Agents

DAAD19-01-1-0560

Abstract

The focus of this research was on introducing advanced concepts from laser technology, controlled quantum dynamics and specialize software to address the problem of detecting chemical and biological agents. This research was initiated at the time when the confluence of these techniques and concepts was beginning to see success in various laboratories. The research performed during the MURI involved a number of interrelated activities concerning optical detection and mass spectrometry with shaped laser pulses acting as a special family of tailored "photonic reagents". The research ranged from basic theoretical developments in the subject of controlling quantum phenomena out through enhancement of the associated laser technology and a variety of key experiments demonstrating the concepts. The research in the MURI made significant advances in laying a rigorous foundation for the creation of a new class of non-linearly functioning detectors of chemical and biological agents. Future R&D in non-linear detection should be able to build on these foundations and take this subject to an advanced level for technology transfer. A summary of these advances under the MURI is given below.

Quantum Wavefunction Controllability, G. Turinici and H. Rabitz, *Chem. Phys.*, 267, 1-9 (2001).

Theoretical results were presented in this work on the ability to arbitrarily steer about a wavefunction for a quantum system under time-dependent external field control. Criteria on the field free Hamiltonian and the field coupling term in the Hamiltonian were presented that assured full wavefunction controllability. Numerical simulations were given to illustrate the criteria. A discussion on the theoretical and practical relationship between dynamical conservation laws and controllability was also included.

Theoretical Considerations for Laser Control of Quantum Systems, H. Rabitz, in *Encyclopedia of Modern Optics*, J.E. Midwinter, A. Miller, and L. Bayvel, eds., Academic Press, United Kingdom (2001).

This work considered the theoretical issues associated with the optimal manipulation of quantum dynamics phenomena. Shaped laser pulses form the primary tool for manipulating quantum systems, and the work focused on both the theoretical design of such pulses, as well as their laboratory discovery using closed loop learning algorithms. A variety of conceptual, numerical, and implementational topics were addressed in presenting the state of this field and its promise for the future.

Closing the Loop on Bond Selective Chemistry Using Tailored Strong Field Laser Pulses, R.J. Levis and H. Rabitz, *J. Phys. Chem. A*, 106, 6427-6444 (2002).

Strong field, closed-loop control of gas phase photochemical reactivity was the focus of this research. The control of chemical reactivity was shown to be possible using tailored

laser pulses to circumvent previous laser bandwidth limitations. As an illustration of this capability, ketone rearrangements and dissociation reactions were considered. To introduce the experiments, we looked at both optimal control theory (OCT) and optimal control experiments (OCE), with an emphasis on closed-loop control methods using near-infrared fs pulses. Because the experiments were in the strong field regime, we reviewed the current state of the understanding of the electronic and nuclear photophysical processes that occur when polyatomic molecules are subjected to laser intensities ranging between 10^{13} and 10^{15} W cm^{-2}. Photoelectron spectroscopy measurements were presented that begin to elucidate the control mechanisms. These delineated the order of the multiphoton process, the presence of transient shifting of excited electronic state energies (on the order of 5 eV), and the phenomena of lifetime broadening of electronic states. Recent experiments probing the energy partitioning to nuclear modes were presented, with an emphasis on detecting the final kinetic energy of fragment ions. The advances in laser pulse shaping technology slaved to pattern recognition learning algorithms have opened up the prospect of studying the dynamics and chemical manipulation of virtually any system that can be introduced into the closed loop apparatus. Rather than operating under the limitation of finding the molecule to suit the laser capabilities, the closed loop learning control procedure operating in the strong field regime made it possible to merely tailor the control laser to meet the molecule's dynamical capabilities, in keeping with the chemical objectives. The prospects are very bright for exploring chemical reactivity with these tools.

Optimal Control of Quantum Systems: Origins of Inherent Robustness to Control Field Fluctuations, H. Rabitz, *Phys. Rev. A,* 66, 063405-1-8 (2002).
The impact of control field fluctuations on the optimal manipulation of quantum dynamics phenomena was investigated in this research. The quantum system was driven by an optimal control field, with the physical focus on the evolving expectation value of an observable operator. A relationship was shown to exist between the system dynamics and the control field fluctuations, wherein the process of seeking optimal performance assured an inherent degree of system robustness to such fluctuations. The presence of significant field fluctuations broke down the evolution of the observable expectation value into a sequence of partially coherent robust steps. Robustness occurred because the optimization process reduced sensitivity to noise-driven quantum system fluctuations by taking advantage of the observable expectation value being bilinear in the evolution operator and its adjoint. The consequences of this inherent robustness were examined in light of recent experiments and numerical simulations on optimal control of quantum phenomena. The analysis in this research bodes well for the future success of closed loop quantum optimal control experiments, even in the presence of reasonable levels of field fluctuations.

Some mathematical and algorithmic challenges in the control of quantum dynamics phenomena, E. Brown and H. Rabitz, *J. Math. Chem.*, 31, 17-63 (2002).
The theory and practice of control over quantum mechanical phenomena is receiving increasing attention, underscored by striking experimental successes. Nevertheless, many questions of fundamental and practical relevance to the field remain unresolved. With the aim of stimulating further development, we formulated a number of theoretical

questions, divided into three categories. First, questions related to control law design were examined, with an emphasis on controllability and optimal control theory. This led to the second category of open problems relevant to closed loop laboratory implementation of quantum control, including learning and feedback methods. The sensitive dependence of control on basic quantum mechanical interactions motivated the third category, which looks at coherent dynamical techniques for identifying the system Hamiltonian. An open issue overarching all of these directions was the need to discover the general rules for the control of quantum systems. Although the list of issues examined in this work is extensive, it should be viewed not as a complete menu for exploration, but rather as a springboard to new challenges, as the field evolves.

Optimal Dynamical Discrimination of Similar Molecules Through Quantum Learning Control, B. Li, G. Turinici, V. Ramakrishna and H. Rabitz, *J. Phys. Chem. B*, 106, 8125-8131 (2002).

This research presented a paradigm for discriminating similar quantum systems in the laboratory, based on optimal control principles with the aid of closed loop learning algorithms. The optimal dynamic discrimination (ODD) process was simulated for a non-interacting mixture of up to three similar finite-dimensional quantum systems. The optimal control field giving rise to species discrimination was deduced with a genetic algorithm (GA), including in the presence of field and observation noise. The similar quantum systems yielded distinct dynamics and detection signals, although influenced by the same control laser pulse. The ODD process was shown to operate by drawing on constructive and destructive interference effects to simultaneously maximize or minimize the signals from each of the species of the mixture. The ODD technique may have applications to the analysis and separation of possibly even complex chemical species.

An Investigation of the effects of Experimental Parameters on the Closed-loop Control of Photoionization/Dissociation Processes in Acetophenone, P. Graham, G. Menkir, R. Levis, *Spec. Acta Part B-Atomic Spectro*.. **58**, 1097 (2003).

The photodissociation channels of acetophenone (C_6H_5)-CO-(CH_3) can be controlled by the use of tailored strong-field laser pulses together with a feedback loop incorporating an adaptive algorithm. This optimal control strategy was used to selectively cleave either the OC-CH_3 or OC-C_6H_5 bonds. Varying either the pulse duration and chirp prior to optimization wss shown to affect the dynamic range of control obtainable. We show that it was possible to decrease the search space by limiting the retardance range of the spatial light modulator (SLM), or by decreasing the number of frequency elements manipulated by the SLM, and still achieve an acceptable degree of control over acetophenone dissociation. Performing consecutive experiments with identical experimental parameters and search criteria reveals that the learning algorithm may find solutions that have the same degree of control with either similar SLM retardances or markedly different retardances. Comparison of the dynamic range of control between single-parameter optimizations (pulse energy and duration) with the tailored electric field profiles generated by the adaptive algorithm revealed an enhancement in the control of reaction product distributions in the latter scheme.

Nonadiabatic Dynamics of Polyatomic Molecules and Ions in Strong Laser Fields, A. Markevitch, S. Smith, N. Moore, H. Schlegel, D. Romanov, M. Ivanov and R. Levis, *Phys. Rev. A*,. 68, (2003).
Ionization and/or fragmentation of large organic molecules in strong laser fields can be quantitatively understood as a transition from adiabatic to nonadiabatic dynamics of the electrons. Measurements of fragmentation patterns demonstrate regular trends as a function of the size and electronic structure of a molecule. The theoretical model agrees quantitatively with the measurements for a series of polycyclic aromatic molecules.

A Local-Time Algorithm for Achieving Quantum Control, F.L. Yip, D.A. Mazziotti and H. Rabitz, *J. Phys. Chem. A*, 107, 7264-7268 (2003).
A local-time algorithm (LTA) is developed for designing electric fields to guide a quantum system toward a desired observable. The LTA is a noniterative forward marching procedure based on making a choice for the control field over the next immediate small time increment t(i+1) - t(i) = Delta solely on the ability of the local field value ε(i) in that increment to take the system closer to the target goal. Each locally optimal field value ε(i), i = 1, 2.... is chosen from a fixed toolkit of discretized members {ε(j)} that sample the dynamic range epsilon(min) less than or equal to epsilon less than or equal to epsilon(max) of the control. Despite the strictly local myopic design process, the LTA is shown to be capable of achieving good quality control results in model systems. The LTA has no fixed time to reach the target, and the time it takes to produce good quality control primarily depends on the "distance" between the initial and target states, as measured by the number of intermediate state linkages connecting them and their strength. A comparison is made between the behavior of optimal control theory (OCT) and the LTA; each has different characteristics, and it is shown that the LTA can be computationally very efficient. LTA and traditional OCT methods can be viewed as extreme cases of a larger class of time-windowed approaches to control.

Quantum Control via Adaptive Tracking, W. Zhu and H. Rabitz, *J. Chem. Phys.*, 119, 3619-3625 (2003).
An adaptive tracking algorithm is developed to achieve quantum system control field designs. The adaptive algorithm has the advantage of operating noniteratively to efficiently find desirable controls, and has the feature of high stability by suppressing the influence of disturbances from tracking singularities. The core of the adaptive tracking control algorithm is a self-learning track switch technique, which is triggered by monitoring of the evolving system trajectory. The adaptive tracking algorithm is successfully tested for population transfer. (C) 2003 American Institute of Physics.

Closed-Loop Quantum Control Utilizing Time Domain Maps, J.S. Biteen, J.M. Geremia and H. Rabitz, *Chem. Phys.*, 290, 35-45 (2003).
Closed-loop laser control of quantum dynamics phenomena may be accomplished through frequency domain manipulations in the laboratory guided by a learning algorithm. This paper presents an alternative method based on the use of nonlinear input output maps generated in the time domain, although the actual experiments and control optimization are carried out in the frequency domain. The procedure first involves the construction of input, output maps relating the field structure to the observed control

performance. These maps are utilized as a substitute for actual experiments in the subsequent optimization stage in order to find the field that drives the system to a specified target. This closed-loop learning process is repeated with a sufficient number of maps until a control field is found that yields the target observable as best as possible. The overall algorithm is simulated with two model quantum systems. It is shown that excellent quality control can be achieved through this sequential learning procedure, even with individual maps that have only modest global accuracy.

Molecular alignment by trains of short laser pulses, M. Leibscher, I. Sh. Averbukh and H. Rabitz, *Phys. Rev. Lett.*, 90, 213001-4 (2003).
We show that a dramatic field-free molecular alignment can be achieved after exciting molecules with proper trains of strong ultrashort laser pulses. Optimal two- and three-pulse excitation schemes are defined, providing an efficient and robust molecular alignment. This opens new prospects for various applications requiring macroscopic ensembles of highly aligned molecules.

The Role of Theory in the Laboratory Control of Quantum Dynamics Phenomena, H. Rabitz, *Theoret. Chem. Accts.*, 109, 64-70 (2003).
Interest in the control of quantum dynamics phenomena has grown in recent years, with laboratory studies showing increasing successes. The role of theory in the control of quantum phenomena encompasses the design of laser controls, the development of algorithms to guide the laboratory studies, and the means to analyze the ensuing dynamics observations. Laboratory laser control instrumentation has the special capability of performing massive numbers of experiments in a short period of time, to rapidly search for controls that meet the objectives. This unique laboratory feature needs to be factored in when considering how to best utilize theoretical analyses. The present paper reviews the role that theory is playing, as well as suggests some future avenues for theory in the laser control of quantum phenomena.

Shaped Laser Pulses as Reagents, H. Rabitz, *Science,* 299, 525-527 (2003).
This paper discussed the concept of intense shaped laser pulses acting as Photonic Reagents. New efforts at extracting mechanistic information from controlled quantum dynamics was also examined.

Quantum Physics under Control, I. Walmsley and H. Rabitz, *Physics Today,* 56, 43-49 (2003).
Thanks to the increasing ability to coherently control quantum systems, designer Hamiltonians can be created to explore new physics and to yield a better understanding of complex phenomena. This paper reviewed the state of these fields.

Quantum Optimally Controlled Transition Landscapes, H. Rabitz, M. Hsieh and C. Rosenthal, *Science,* 303, 998 (2004).
A large number of experimental studies and simulations show that it is surprisingly easy to find excellent quality control over broad classes of quantum systems. We now prove that for controllable quantum systems with no constraints placed on the controls, the only allowed extrema of the transition probability landscape correspond to perfect control or no control. Under these conditions, no suboptimal local extrema exist as traps that would

impede the search for an optimal control. The identified landscape structure is universal for all controllable quantum systems of the same dimension when seeking to maximize the same transition probability, regardless of the detailed nature of the system Hamiltonian. The presence of weak control field noise or environmental decoherence is shown to preserve the general structure of the control landscape, but at lower resolution.

Shaped Laser Pulses Acting as Photonic Reagents, H. Rabitz, in *Ultrafast Molecular Events in Chemistry and Biology*, M. M. Martin and J. T. Hynes, eds. (Elsevier), 2004.

In recent years, great strides have been made in controlling quantum phenomena through the use of tailored laser pulses. These shaped pulses interact with molecules in a manner acting effectively as reagents with fleeting existence, yet they may have a lasting dynamical impact on a molecule or material. This paper discusses the basic concepts of quantum control, especially drawing on the ability to perform massive numbers of closed loop control experiments. Particular attention is given to the prospect of deducing control mechanisms and the introduction of special closed loop control techniques to reveal Hamiltonian information. Recent computations and experiments point to an increasing ability to control and understand quantum systems through closed loop laboratory techniques.

Mechanistic Analysis of Optimal Dynamic Discrimination of Similar Quantum Systems, A. Mitra and H. Rabitz, *J. Phys. Chem. A.*, 108, 4778 (2004).

Optimal dynamic discrimination (ODD) was recently introduced as technique for maximally drawing out and detecting the differences between similar quantum systems by exploiting their controllable dynamical properties. As a simulation of ODD, optimal fields were found that successfully discriminated amongst similar species, but the underlying mechanisms of the process remained obscure. Hamiltonian encoding (HE) has been introduced as technique for identifying the mechanisms of controlled quantum dynamics. The results of a HE based simulation analysis of ODD is presented in this paper. Different types and degrees of constructive and destructive interference are shown to underlie the controlled discrimination processes. In general, it is found that successful discrimination relies on more complex interfering pathways for increasing similar systems, or increasing numbers of similar quantum systems.

Optimal Discrimination of Multiple Quantum Systems: Controllability Analysis, G. Turinici, V. Ramakrishna, B. Li and H. Rabitz, *J. Phys. A*, 37, 273-282 (2004).

A theoretical study is presented concerning the ability to dynamically discriminate between members of a set of different (but possibly similar) quantum systems. This discrimination is analyzed in terms of independently and simultaneously steering about the wavefunction of each component system to a target state of interest using a tailored control (i.e. laser) field. Controllability criteria are revealed and their applicability is demonstrated in simple cases. Discussion is also presented in some uncontrollable cases.

Optimal Control of Quantum Non-Markovian Dissipation: Reduced Liouville-Space Theory, R. Xu, Y.J. Yan, Y. Ohtsuki, Y. Fujimura and H. Rabitz, *J. Chem. Phys.*, 120, 6600 (2004).

An optimal control theory for open quantum systems is constructed containing non-Markovian dissipation manipulated by an external control field. The control theory is

developed based on a novel quantum dissipation formulation that treats both the initial canonical ensemble and the subsequent reduced control dynamics. An associated scheme of backward propagation is presented, allowing the efficient evaluation of general optimal control problems. As an illustration, the control theory is applied to the vibration of the hydrogen fluoride molecule embedded in a non-Markovian dissipative medium. The importance of control-dissipation correlation is evident in the results.

Cooperating or Fighting with Noise in the Optimal Control of Quantum Dynamics, F. Shuang, M. Dykman and H. Rabitz, *J Chem. Phys*., 121, 9270-9278 (2004).
This paper investigates the impact of control field noise on the optimal manipulation of quantum dynamics. Simulations are performed on several multilevel quantum systems with the goal of population transfer in the presence of significant control noise. A genetic algorithm with an improved elitism operator is used to find the optimal field that either fights against or cooperates with control field noise. When seeking a high control yield it is possible to find fields that successfully fight with the noise while attaining good quality stable results. When seeking modest control yields, fields can be found which are optimally shaped to cooperate with the noise and thereby drive the dynamics more efficiently. In general, noise reduces the coherence of the dynamics, but the results indicate that population transfer objectives can be met by appropriately either fighting or cooperating with noise, even when it is intense.

Optimal Quantum Control with Multi-Polarization Fields, R. Wu, I. Solá, and H. Rabitz, *Chem. Phys. Let*, 400, 469-475 (2004).
The dynamical advantages for employing up to three independently shaped polarization fields are explored in the optimal control of quantum systems. The analysis compares multi-polarization optimal control with what may be achieved using linearly polarized (1-D) control. Simulations on a model system show how multi-polarization (2-D, 3-D) optimally shaped pulses can overcome symmetry forbidden transitions and improve control quality by better accessibility o the target state.

Coulomb Explosion Assisted by Nonadiabatic Charge Localization, A. Markevitch, D. Romanov, S. Smith and R. Levis, Phys. Rev. Lett. 92, 033002 (2004).
The electron-nuclear dynamics of Coulomb explosion of a large polyatomic molecule, anthracene, is probed using kinetic energy distributions of produced H^+ ions. The kinetic energy release of ejected protons exceeds 30 eV for anthracene exposed to 10^{14} $W \cdot cm^{-2}$, 800 nm pulses of 60 fs duration. We propose a strong-field charge localization model, based on nonadiabatic dynamics of charge distribution in a (multiply) ionized molecule; the charge localization lasts many laser periods and is sustained through successive ionizations of the molecular ion. The model explains quantitatively the dependence of the H^+ kinetic energy on the laser intensity. Dissociative ionization of a polyatomic molecule enabled by long-lived charge localization is a new type of electron-nuclear dynamics and is essential for understanding the pathways of molecular/ionic fragmentation in strong fields.

Fragmentation pathways in a series of CH3COX molecules in the strong field regime, S. Anand, M. Zamari, G. Menkir, and R. Levis, *J. Phys. Chem. A*, 108, 3162 (2004).

In intense laser fields, fragment ions can be produced from CH3COX (X = CH3, CF3, and C6H5) either by absorption and dissociation followed by ionization (ADI) or absorption and ionization followed by dissociation (AID). Electronic structure calculations were carried out using Hartree-Fock, density functional, and correlated levels of theory to understand the possible fragmentation pathways. The calculated ionization potentials are in very good agreement with the available experimental data. For acetone, the acetyl ion is predicted to be the most preferred dissociation product and can be produced by either mechanism. The very low C-CF3 bond energy in the parent ion of trifluoroacetone provides a clear reason for the absence of CF3COCH3+ and CF3CO+ ion peaks from the mass spectrum of CF3COCH3 after intense laser excitation and indicates that fragmentation occurs by AID. For acetophenone, both CH3CO+ and C6H5CO+ are stable fragments, with the latter being produced by an AID mechanism.

Sequential nonadiabatic excitation of large molecules and ions driven by strong laser fields, A.N. Markevitch, D.A. Romanov, S.M. Smith, and R. Levis, *Phys. Rev, A*, 69, 013401 (2004).

Electronic processes leading to dissociative ionization of polyatomic molecules in strong laser fields are investigated experimentally, theoretically, and numerically. Using time-of-flight ion mass spectroscopy, we study the dependence of fragmentation on laser intensity for a series of related molecules and report regular trends in this dependence on the size, symmetry, and electronic structure of a molecule. Based on these data, we develop a model of dissociative ionization of polyatomic molecules in intense laser fields. The model is built on three elements: (i) nonadiabatic population transfer from the ground electronic state to the excited-state manifold via a doorway (charge-transfer) transition; (ii) exponential enhancement of this transition by collective dynamic polarization of all electrons, and (iii) sequential energy deposition in both neutral molecules and resulting molecular ions. The sequential nonadiabatic excitation is accelerated by a counterintuitive increase of a large molecule's polarizability following its ionization. The generic theory of sequential nonadiabatic excitation forms a basis for quantitative description of various nonlinear processes in polyatomic molecules and ions in strong laser fields.

Static and Dynamic Polarizabilities of Conjugated Molecules and their Cations, S. M. Smith, A. Markevitch, D. Romanov, X. Li, R. Levis and H. B. Schlegel, J. *Phys. Chem.* 108, 11063 (2004).

Recent advances in strong-field chemistry highlight the need for calculated properties of molecules and their molecular ions for which no experimental values exist. Both static and frequency-dependent properties are required to understand the dynamics of laser-molecule (ion) coupling. It is particularly important to understand the dynamics of the optical response of multi-electron systems in the near IR (~ 800 nm) region, where the majority of strong-field experiments are performed. To this end we calculated ground state first-order polarizabilities (a) and excitation energies for two series of conjugated organic molecules and their molecular ions: (a) trans linear polyenes ranging in size from butadiene (C_4H_6) to octadecanonene ($C_{18}H_{20}$) and (b) polyacenes ranging in size from

benzene (C_6H_6) to tetracene ($C_{18}H_{12}$). The major observed trends are: (i) a increases nonlinearly with molecular size, (ii) for larger systems a significantly increases upon ionization, and (iii) for larger ions, dynamic a is much larger than static. We discuss the size scaling and frequency dependence of , and provide simple models that capture the origin of the change in upon ionization.

Optimally controlling the internal dynamics of a randomly orientated ensemble of molecules, G. Turinici and H. Rabitz, *Phys. Rev. A*, 70, 063412 (2004). The ultra-fast control of large polyatomic molecules in the gas and condensed phases entails working with a randomly orientated ensemble. During the short control period, little reorientation may occur especially for cases in the condensed phases. This paper addresses the degree to which all members of the ensemble may be simultaneously controlled with respect to their internal motion by a single laser pulse. It is shown that all members of the ensemble are fully controllable if any one member is. Numerical optimal control simulations also show that excellent quality full ensemble control can be achieved even with reasonable constraints placed on the control fields. Although the full ensemble may be controlled to a high degree, the control mechanism is likely to differ for each ensemble member.

Connectivity analysis of quantum control, R. Wu, H. Rabitz, G. Turinici and I. Sola, *Phys. Rev. A*, 70, 052507 (2004). A connectivity analysis of controlled quantum systems assesses the feasibility of a field existing that can transfer at least some amplitude between any specified pair of states. Although Hamiltonians with special structure or symmetry may not produce full connectivity, it is argued and demonstrated that virtually any Hamiltonian is expected to be connected. The connectivity of any particular system is generally revealed in the quantum evolution over a single or at most a few time steps. A connectivity analysis is inexpensive to perform and it can also identify statistically significant intermediate states linking a specified initial and final state. These points are illustrated with several simple systems. The likelihood of any arbitrary system being connected implies that at least some product yield can be expected in the laboratory for virtually all systems subjected to a suitable control.

Femtosecond laser pulses distinguish bacteria from background urban aerosols, F. Courvoiser, V. Boutou, V. Wood, J.-P. Wolf, A. Bartelt, M. Roth, H. Rabitz, *Appl. Phys. Lett*, 87, 063901 (2005).
The fluorescence from living bacteria Bacillus subtilis, Enteroccocus and Escherichia coli, induced by a ultrashort 270 nm pump pulse is depleted up to 50% by an optically delayed ultrafast 810 nm probe pulse in a pump-probe arrangement. The fast subpicosecond fluorescence decrease occurs for a pump-probe delay of t 2 ps. Depletion is also observed for tryptophan in water in contrast with organic cyclic molecules such as naphtalene or diesel fuel, despite similar absorption and fluorescence spectra. This remarkable difference allows us to propose a new remote sensing method able to efficiently discriminate organic from biological aerosols in highly populated urban areas.

Time-Dependent Hartree-Fock Approach for Studying the Electronic Optical Response of Molecules in Intense Fields, X. Li, S.M. Smith, A. Markevitch, D. Romanov, R. Levis and H. B. Schlegel, *Chem. Chem. Phys.*, 7, 233 (2005).

The time-dependent Hartree-Fock (TDHF) method is used to simulate the electronic behavior of molecules in high intensity oscillating electric fields, where a perturbative approach is no longer valid. A unitary transform approach is combined with the modified midpoint method to provide a stable and efficient algorithm to integrate the TDHF equations for the electronic density of molecules represented in an atom-centered basis. The behavior of H_2^+ in an intense oscillating filed computed using the TDHF method with a STO-3G basis set is in excellent agreement with the analytically solvable two-state coherent excitation model. For H_2 in an oscillating field of 3.5×10^{14} W/cm^2 and 760 nm, TDHF simulations with a 6-311++G(d,p) basis set show that the molecular orbital energies, electron populations, and atomic charges follow the field adiabatically. As the field intensity is increased, the response becomes more complicated as a result of contributions from higher lying states. The TDHF results are nearly indistinguishable from calculations using the full time-dependent Schrödinger equation. Simulations of N_2 in the same field show even greater complexity, yet the average charge still follows the field adiabatically,

Cooperating or Fighting with Decoherence in the Optimal Control of Quantum Dynamics, F. Shuang and H. Rabitz, *J. Chem. Phys.*, 124, 154105 (2006).

This paper explores the use of laboratory closed-loop learning control to either fight or cooperate with decoherence in the optimal manipulation of quantum dynamics. Simulations of the processes are performed in a Lindblad formulation on multilevel quantum systems strongly interacting with the environment without spontaneous emission. When seeking a high control yield it is possible to find fields that successfully fight with decoherence while attaining a good quality yield. When seeking modest control yields, fields can be found which are optimally shaped to cooperate with decoherence and thereby drive the dynamics more efficiently. In the latter regime when the control field and the decoherence strength are both weak, a theoretical foundation is established to describe how they cooperate with each other. In general, the results indicate that the population transfer objectives can be effectively met by appropriately either fighting or cooperating with decoherence.

Quantum Optimal Control: Hessian analysis of the control landscape, Z. Shen, M. Hsieh and H. Rabitz, *J. Chem. Phys.*, 124, 204106 (2006).

Seeking an effective quantum control entails searching over a landscape defined as the objective as a functional of the control field. This paper considers the problem of driving a state-to-state transition in a finite level quantum system, and analyzes the local topology of the landscape of the final transition probability in terms of the variables specifying the control field. Numerical calculation of the eigenvalues of the Hessian of the transition probability with respect to the control field variables reveals systematic structure in the spectra reflecting the existence of a generic and simple control landscape topology. An illustration shows that the number of nonzero Hessian eigenvalues is determined by the number of quantum states in the system. The Hessian eigenvectors associated with its nonzero eigenvalues are shown to give insight into the cooperative roles of the control

variables. The practical consequences of these findings for quantum control are discussed.

Exploring the level sets of quantum control landscapes, A. Rothman, T.-S. Ho and H. Rabitz*, Phys. Rev. A*, 73, 053401 (2006).
A quantum control landscape is defined by the value of a physical observable as a functional of the time-dependent control field E for a given quantum-mechanical system. Level sets through this landscape are prescribed by a particular value of the target observable at the final dynamical time T, regardless of the intervening dynamics. We present a technique for exploring a landscape level set, where a scalar variable s is introduced to characterize trajectories along these level sets. The control fields E , t accomplishing this exploration are determined by solving a differential equation over s in conjunction with the time-dependent Schrödinger equation. There is full freedom to traverse a level set, and a particular trajectory is realized by making an a priori choice for a continuous function f , t that appears in the differential equation for the control field. The continuous function f , t can assume an arbitrary form, and thus a level set generally contains a family of controls, where each control takes the quantum system to the same final target value, but produces a distinct control mechanism. In addition, although the observable value remains invariant over the level set, other dynamical properties are not specifically preserved and can vary greatly. Examples are presented to illustrate the continuous nature of level-set controls and their associated induced dynamical features, including continuously morphing mechanisms for population control in model quantum systems.

Quantum optimal control of molecular isomerization in the presence of competing dissociation channel, M. Artamonov, T.-S. Ho., H. Rabitz*, J. Chem. Phys.*, 124, 064306, (2006).
The quantum optimal control of isomerization in the presence of a competing dissociation channel is simulated on a two-dimensional model. The control of isomerization of a hydrogen atom is achieved through vibrational transitions on the ground-state surface as well as with the aid of an excited-state surface. The effects of different competing dissociation channel configurations on the isomerization control are explored. Suppression of the competing dissociation dynamics during the isomerization control on the ground-state surface becomes easier with an increase in the spatial separation between the isomerization and dissociation regions and with a decrease in the dissociation channel width. Isomerization control first involving transfer of amplitude to an excited-state surface is less influenced by the dissociation channel configuration on the ground-state surface, even in cases where the excited-state surface allows for a moderate spreading of the excited

Quantum optimal control of HCN isomerization, M. Artamonov, T.-S. Ho, and H. Rabitz*, Chem. Phys.*, 328, 147 (2006).
Quantum optimal control of HCN isomerization is studied including all vibrational degrees of freedom and with rotation treated in the sudden approximation. The nuclear dynamics toolkit (NDT) technique is used for solving the control equations. The NDT is shown to be successful in reducing the computational expense in the large-scale optimal

control calculations by shifting the resource burden from the processor to the storage. The C--N stretching mode was found to be important in the isomerization dynamics. Modest isomerization yields were found when keeping the field intensity below levels where severe electronic disturbances could occur. Significant molecular orientational dependence upon the yield is found, with some orientations producing high yields while others giving little product when exposed to a single optimal field.

Teaching the environment to control quantum systems, A. Pechen, H. Rabitz, *Phys. Rev. A*, 73, 062102 (2006).
A non-equilibrium, generally time-dependent, environment whose form is deduced by optimal learning control is shown to provide a new means for incoherent manipulation of quantum systems. Incoherent control by the environment (ICE) can serve to steer a system from an initial state to a target state, either mixed or in some cases pure, by exploiting dissipative dynamics. Implementing ICE with either incoherent radiation or a gas as the control is explicitly considered, and the environmental control is characterized by its distribution function. Simulated learning control experiments are performed with simple illustrations to find the shape of the optimal non-equilibrium distribution function that best affects the posed dynamical objectives.

Observation-Assisted optimal control of quantum dynamics, F. Shuang, A. Pechen, T.-S. Ho, H. Rabitz, *J. Chem. Phys.*, 126, 134303 (2007).
This paper explores the utility of instantaneous and continuous observations in the optimal control of quantum dynamics. Simulations of the processes are performed on several multilevel quantum systems with the goal of population transfer. Optimal control fields are shown to be capable of cooperating or fighting with observations to achieve a good yield, and the nature of the observations may be optimized to more effectively control the quantum dynamics. Quantum observations also can break dynamical symmetries to increase the controllability of a quantum system. The quantum Zeno and anti-Zeno effects induced by observations are the key operating principles in these processes. The results indicate that quantum observations can be effective tools in the control of quantum dynamics.

Adaptive control of the spatial position of white light filaments in an aqueous solution, G. Heck, J. Sloss, R. Levis, Opt. Com., 259, 216 (2006).
We demonstrate control over the spatial coordinates (position and extent) of white light filaments (supercontinuum generation) in an aqueous solution. These are the first experiments to achieve control of filament position through the manipulation of the spectral phase of an ultra-fast (50 fs) 800 nm excitation laser pulse. A closed feedback loop employing a spatial light modulator and a genetic algorithm was used to manipulate the spectral phase of the pulses to achieve a specified filament position and length.

Rapid Proton Transfer Mediated by a Strong Laser Field, A. Markevitch, D. Romanov, S. Smith, and R. Levis, Phys. Rev. Lett., 96, 163002 (2006).
Kinetic energy distributions of H ejected from a polyatomic molecule, anthraquinone, subjected to 60 fs, 800 nm laser pulses of intensity between 0.2 and 4:0 10^{14} W/cm^2, reveal field-driven restructuring of the molecule prior to Coulomb explosion.

Calculations demonstrate fast intramolecular proton migration into a field-dressed metastable potential energy minimum. The proton migration occurs in the direction perpendicular to the polarization of the laser field. Rapid field-mediated isomerization is an important new phenomenon in coupling of polyatomic molecules with intense lasers.

Assessing and managing laser system stability for quantum control experiments, M. Roth, J. Roslund, H. Rabitz, *Rev. Sci. Inst.* , 77, 083107 (2006). Stable laser operation, which is essential for quantum control experiments as well as many other phase dependent processes, is investigated with respect to the influence of amplitude and spectral phase noise. Simulations are first performed and an easy to implement experimental method is presented to monitor the amplitude and phase stability of an ultrafast laser system. As an illustration of this stability assessment technique, the data monitoring is used to guide the identification and elimination of fluctuations in the laser amplification process. Through a number of practical alterations of the amplifier configuration the stability of the laser system was greatly and consistently improved. Fluctuations on different timescales were eliminated, with special emphasis given to maintaining a stable spectral phase.

Pump-Probe depletion spectroscopy for discriminating organic and biological molecules, F. Courvoisier, V. Boutou, V. Wood, J-P Wolf, A. Bartelt, M. Roth and H. Rabitz, submitted *Science*
The fluorescence from living bacteria (Bacillus Subtilis, Enteroccocus and Escherichia Coli), induced by a ultrashort 270 nm pump-pulse is depleted up to 50 percent by an optically delayed ultrafast 800 nm probe-pulse in a pump-probe arrangement. The fast (subpicosecond) fluorescence decrease occurs for a pump-probe delay of $\Delta t > 2$ps. Depletion is also observed for Trp in water in contrast with organic molecules such as Naphtalene or diesel fuel, despite similar absorption and fluorescence spectra. This remarkable difference allows us to propose a new remote sensing method able to efficiently discriminate organic from biological aerosols.

Control Goal Selection through Anti-Correlation Analysis in the Detection Space. Huyen T. Tran, Dmitri A. Romanov, Robert J. Levis, *J. Phys. Chem. A*, 110, 10558 (2006).
A statistical method is reported to determine the pairs of fragment ions in a mass spectrum that are most susceptible to control by adaptive optimization of the laser pulse shapes in the strong-field regime. The proposed method is based on covariance analysis of the mass spectral fragmentation patterns generated by a set of random shaped pulses. The pairs of fragmentions that have higher negative covariances possess a correspondingly higher degree of controllability in an adaptive control experiment, while the pairs that have higher positive covariances possess correspondingly lower controllability.

Laboratory observation of quantum control level sets, J. Roslund, M. Roth, H. Rabitz, *Phys. Rev. A*, 74, 043414 (2006).
In controlled quantum dynamics, a level set is defined as the collection of control fields that produce a specific value for a particular observable. This paper explores the

relationship between individual solutions to a control problem, and presents the first experimentally observed quantum control level sets, which are found to be continuous submanifolds. Level sets are observed for two photon transitions where the control is the spectral phase function, which is expressed as a fourth-order polynomial. For the systems studied here, the level sets are shown to be closed surfaces in the spectral phase control space. A perturbation analysis provides insight into the observed topology of the level set, which is shown to be preserved by the low-order polynomial phase representation. Each of the multiple control fields forming a level set preserves the observable value by its own distinct manipulation of constructive and destructive quantum interferences. Thus, the richness of quantum control fields meeting a particular observable value is accompanied by an equally diverse family of control mechanisms.

Probing strong-field electron-nuclear dynamics of polyatomic molecules using proton motion, A. Markevitch, D. Romanov, S. Smith, R. Levis, *Phys. Rev. A.* 75, 053402 (2007).

Proton ejection during Coulomb explosion is studied for several structure-related organic molecules (anthracene, anthraquinone, and octahydroanthracene) subjected to 800 nm, 60 fs laser pulses at intensities from 0.50 to $4.0X10^{14}$ W cm^{-2}. The proton kinetic energy distributions are found to be markedly structure specific. The distributions are bimodal for anthracene and octahydroanthracene and trimodal for anthraquinone. Maximum (cutoff) energies of the distributions range from 50 eV for anthracene to 83 eV for anthraquinone. The low-energy mode (~ 10 eV) is most pronounced in octahydroanthracene. The dependence of the characteristic features of the distributions on the laser intensity provides insights into molecular specificity of such strongfield phenomena as (i) nonadiabatic charge localization and (ii) field-mediated restructuring of polyatomic molecules polarized by a strong laser field.

A numerical simulation of non-adiabatic electron excitation in the strong-field regime: 3. Polyacene Neutrals and Cations, S. Smith, X. Li, A. Markevitch, D. Romanov, R. Levis, H. Schlegel, *J. Phys. Chem. A.* 111, 6920 (2007).

The electron optical response for a series of linear polyacenes and their molecular ions (mono and dications) in strong laser fields was studied using time-dependent Hartree-Fock theory. The interactions of benzene, naphthalene, anthracene, and tetracene with pulsed fields at a frequency of 1.55 eV and intensities of 8.77×10^{13}, 3.07×10^{13}, 1.23×10^{13}, and 2.75×10^{12} W/cm^2, respectively, were calculated using the 6-31G(d,p) basis set. Nonadiabatic processes, including nonadiabatic time evolution of the dipole moment, Löwden charges, and occupation numbers, were studied. The nonadiabatic response increased with the length of the molecule and was greatest for the molecular monocations. The only exception was tetracene, in which the very strong response of the dication was due to a near resonance with the applied field. The intensity and frequency dependence of the dipole moment response for the monocations of naphthalene and anthracene was also calculated. As the intensity increased, the population of higher-energy excited-states increased, and as the frequency increased, the excitation volume increased in good agreement with the Dykhne approximation.

Adaptive femtosecond pulse shaping to control supercontinuum generation in a microstructure fiber, D. Lorenc, D. Velic, A. Markevitch, R. Levis, R. J., *Opt. Comm.*, 276, 288 (2007).

Efficient confinement of laser radiation in the core of a photonic crystal fiber increases the nonlinear processes resulting in supercontinuum generation. The technique of adaptive pulse shaping using an evolutionary algorithm provides a method to gain control over such highly nonlinear processes. Adaptive pulse shaping of the driving laser radiation passing through the photonic crystal fiber is employed to modify the shape and composition of the output supercontinuum. Amplitude and phase shaping are used to optimize the broadband emission between 500 and 700 nm, as well as a soliton centered at 935 nm. The intensities of the emission and of the soliton driven by a shaped laser pulse increase in comparison to an unshaped pulse by factors of 4 and 3, respectively. The spectral width in the range of 500–600 nm is increased by approximately 40%. In addition, the suppression of self-steepening effects in supercontinuum spectra is demonstrated.

Quantum control mechanism analysis through field based Hamiltonian encoding: A laboratory implementable algorithm, A. Mitra and H. Rabitz, *J. Chem. Phys.*, 120, 044112 (2008).

Optimal control of quantum dynamics in the laboratory is proving to be increasingly successful. The control fields can be complex, and the mechanisms by which they operate have often remained obscure. Hamiltonian encoding (HE) has been proposed as a method for understanding mechanisms in quantum dynamics. In this context mechanism is defined in terms of the dominant quantum pathways leading to the final state of the controlled system. HE operates by encoding a special modulation into the Hamiltonian and decoding its signature in the dynamics to determine the dominant pathway amplitudes. Earlier work encoded the modulation directly into the Hamiltonian operators. This present work introduces the alternative scheme of field based HE, where the modulation is encoded into the control field and not directly into the Hamiltonian operators. This distinct form of modulation yields a new perspective on mechanism and is computationally faster than the earlier approach. Field based encoding is also an important step towards a laboratory based algorithm for HE as it is the only form of encoding that may be experimentally executed. HE is also extended to cover systems with noise and uncertainty and finally, a hierarchical algorithm is introduced to reveal mechanism in a stepwise fashion of ever increasing detail as desired. This new hierarchical algorithm is an improvement over earlier approaches to HE where the entire mechanism was determined in one stroke. The improvement comes from the use of less complex modulation schemes, which leads to fewer evaluations of Schrödinger's equation. A number of simulations are presented on simple systems to illustrate the new field based encoding technique for mechanism assessment.

Multicomponent Control via Shaped, Strong Laser Fields Mass Spectroscopy, L. Palliyaguru, J. Sloss, H. Rabitz, R Levis, *J.Mod. Optics*, 55, 177 (2008).

The fragmentation processes of polyatomic molecules induced by an intense laser field exhibit sensitive dependence on the laser characteristics such as intensity, pulse duration,

wavelength, and shape of the temporal pulse envelope. Adaptive laser pulse shaping can control the fragmentation of methyl/methoxy groups in dimethyl methylphosphonate (DMMP), a simulant for nerve agent Sarin. The exploitation of the sensitivity of molecular fragmentation to laser pulse shapes represents a new way to discriminate molecular identity. Here we have shown manipulation of branching ratio M-$(OCH_3)^+$/M-$(CH_3)^+$, M-2$(CH_3)^+$/M-$(CH_3)^+$ and M-$(OCH_3)^+$/M-2$(CH_3)^+$ fragment ion ratios for DMMP in the presence of complex background in the extraction region of TOF spectrometer using tailored femtosecond laser pulses. We suggest that the use of adaptive femtosecond laser pulse shaping coupled to TOF mass spectrometry is an accurate way to identify complex airborne organophosphate molecules similar to nerve agents.

Adaptive reshaping of objects in (multiparameter) Hilbert space for enhanced detection and classification: an application of receiver operating curve statistics to laser-based mass spectroscopy, D. Romanov, D. Healy, J. Brady, R. Levis, *J. Opt. Soc. Am. A.*, 25, (2008).

We propose a new approach to the classical detection problem of discrimination of a true signal of interest from an interferent signal, which may be applied to the area of chemical sensing. We show that the detection performance, as quantified by the receiver operating curve (ROC), can be substantially improved when the signal is represented by a multicomponent data set that is actively manipulated by means of a shaped laser probe pulse. In this case, the signal sought (agent) and the interfering signal (interferent) are visualized by vectors in a multidimensional detection space. Separation of these vectors can be achieved by adaptive modification of a probing laser pulse to actively manipulate the Hamiltonian of the agent and interferent. We demonstrate one implementation of the concept of adaptive rotation of signal vectors to chemical agent detection by means of strong-field time-of-flight mass spectrometry.

Measuring the spatiotemporal electric field of ultrashort pulses with high spatial and spectral resolution, P. Bowlan, P. Gabolde, M. Coughlan, R. Trebino, and R. Levis, *J. Opt. Soc. Am. B*, 25, (2008).

We demonstrate an experimentally simple and high-spectral-resolution version of spectral interferometry (SEA TADPOLE) that can measure complicated pulses (in time) at video rates. Additionally, SEA TADPOLE can measure spatial information about a pulse, and it is the first technique that can directly measure the spatiotemporal electric field *_E_x,y,z,___* of a focusing ultrashort pulse. To illustrate and test SEA TADPOLE, we measured *E___* of a shaped pulse that had a time–bandwidth product of approximately 100. To demonstrate that SEA TADPOLE can measure focusing pulses, we measured *E_x,__* at and around the focus produced by a plano–convex lens. We also measured the focus of a beam that had angular dispersion present before the lens. We have found that SEA TADPOLE can achieve better spectral resolution than an equivalent spectrometer, and here we discuss this in detail, giving both experimental and simulated examples. We also discuss the angular acceptance and spatial resolution of SEA TADPOLE when measuring the spatiotemporal field of a focusing pulse.

Identification of biological microparticles using ultrafast depletion spectroscopy, F. Courvoisier, L. Bonacinia, V. Boutou, B. Thuillier, J. Extermann, M. Roth, H.

Rabitz and HP Wolf, *Faraday Discuss.*, 137, 37, (2008).
This research shows how an ultrafast pump - pump excitation induces strong fluorescence depletion in biological samples, such as bacteria- containing droplets, in contrast with fluorescent interferents, such as polycyclic aromatic compounds, despite similar spectroscopic properties. Application to the optical remote discrimination of biotic versus non- biotic particles is proposed. Further improvement is required to allow the discrimination of one pathogenic among other non- pathogenic micro- organisms. This improved selectivity may be reached with optimal coherent control experiments, as discussed in the paper.

Understanding the role of representation in controlled quantum-dynamical mechanism analysis, A. Mitra, I. Sola and H. Rabitz, *Phys. Rev. A*, 77, 043415 (2008).
Hamiltonian Encoding (HE) has been proposed as a technique for analyzing the mechanism of controlled quantum dynamics, where mechanism is understood in terms of the set of amplitudes of the dominant pathways connecting the initial and final states of the system. The choice of representation for the system wave function is often motivated by seeking simplicity for the structure of the Hamiltonian and not necessarily for the generated dynamics. However, the mechanism revealed by HE is strongly dependent on the basis in which the wave function is represented. The degree of mechanistic complexity is indicated by the relevant orders of the Dyson series contributing to the dynamics. An appropriate choice of representation can yield a simpler view of the dynamical mechanism by shifting some of the complexity into the representation itself. In this work the choice of representation is set up as the solution to a variational optimization problem. For unconstrained basis transformations, the optimization of the representation is formally equivalent to solving the time-dependent Schrodinger equation; different constrained basis transformations provide distinct dynamical perspectives. Specific constrained variational Ansatze are compared and analyzed by performing HE on several simple Hamiltonians with an observation of the extent to which the mechanism assessment varies with representation. The general variational formulation for determining representation can flexibly admit other Ansatze with the ultimate aim of balancing the ease of determining and understanding the representation with the reduction in mechanistic complexity.

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Alexei Markevitch, Graduate Student
Bernard Schlegel, Professor of Chemistry
Stanley Smith, Post-Doctoral Associate
Muhannad Zamari, Graduate Student
Ilya Greenberg, Computer Consultant
Getahun Menkir, Graduate Student
Lalinda Palliyaguru, Graduate Student
Ryan Compton, Graduate Student
Matt Coughlan, Graduate Student
Benjamin Bui, Undergraduate student
Ruth Elliott, Undergraduate student
Josh Meyer, Undergraduate student
Joseph Sloss, Undergraduate student
Huyen Tran, Undergraduate student

Report of inventions (by title only):

1. Quantum Dynamic Discriminator of Molecular (Chemical and Biological) Agents, H. Rabitz and R. Levis
2. Apparatus and software for assessing the stability of the spectral phase of ultra-short laser systems on time-scales ranging from shot-to-shot to the entire operating time, H. Rabitz